SELECTIVE LASER ABLATION IN RESISTS AND BLOCK COPOLYMERS FOR HIGH RESOLUTION LITHOGRAPHIC PATTERNING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This U.S. Utility Application claims priority to U.S. Provisional Application Ser. No. 62/164,823 filed May 21, 2015, which application is incorporated herein by reference as if fully set forth in their entirety.

STATEMENT OF GOVERNMENTAL SUPPORT

[0002] The invention described and claimed herein was made in part utilizing funds supplied by the U.S. Department of Energy under Contract No. DE-ACO2-05CH11231 between the U.S. Department of Energy and the Regents of the University of California for the management and operation of the Lawrence Berkeley National Laboratory. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

Field of the Invention

[0003] Block copolymer lithography (BCPL) offers an appealing option for patterning structures at the 3-30 nm size scale. Industrial applications for semiconductor chip manufacturing and hard drives are on the horizon, but as noted in a recent review by Bates, et. al. will require overcoming challenges in many areas, including pattern transfer. As noted in the review by Gu, et. al., there are two critical steps in BCPL pattern transfer, selective removal of one block and then transferring the pattern left by the remaining block to the substrate. In this paper we focus on the first step, selective block removal.

[0004] Plasma based dry etching (i.e. reactive-ion etching, RIE) is typically used for block removal over wet etching because it avoids pattern distortion/collapse caused by capillary forces in the wet block removal approach, as shown in the polystyrene-b-polymethylmethacrylate (PS-b-PMMA) system. However, not all block copolymer systems have selectivity in plasma-based chemistries and alternatives approaches need to be developed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. **1** illustrates laser ablation for protected and deprotected poly((t-butoxycarbonyloxy)styrene (BOCS).

[0006] FIGS. **2**A, **2**B, **2**C and **2**D illustrate images of selectively ablated PHOST from a PS-b-PHOST 46 nm in pitch. FIGS. **2**A illustrates an AFM image. FIGS. **2**B illustrates an AFM line scan of FIGS. **2**A. FIGS. **2**B illustrates an SEM image. Scale bar is 200 nm. FIGS. **2**D illustrates an SEM overview of an ablated area, the lighter area is where ablation occurs.

[0007] FIG. **3** illustrates AFM images of P2VP-b-PS-b-P2VP with a 20 nm pitch.

[0008] FIG. **4** illustrates a SEM image of ablated 10 nm half-pitch PS-b-PVP complexed with platinum.

DETAILED DESCRIPTION

[0009] In the discussions that follow, various process steps may or may not be described using certain types of manufacturing equipment, along with certain process parameters. It is to be appreciated that other types of equipment can be used, with different process parameters employed, and that some of the steps may be performed in other manufacturing equipment without departing from the scope of this invention. Furthermore, different process parameters or manufacturing equipment could be substituted for those described herein without departing from the scope of the invention.

[0010] Various embodiments of the invention describe the selective laser ablation process for block copolymer lithography (BCPL) in three systems where there is difficulty using traditional reactive ion etch (RIE) to remove one block selectively, specifically : polystyrene-b-polyhydroxyl-styrene (PS-b-PHOST), poly-2-vinylpyridine-b-polystyrene-b-poly-2-vinylpyridine (P2VP-b-PS-b-P2VP), and P2VP-b-PS-b-P2VP where the P2VP is infiltrated with platinum. For neat BCPs, even if, e.g., they are microphase separated, the aromatic nature of the monomers makes the plasma etching rates similar. Two alternative methods have emerged to increase etch selectivity between blocks. One method includes selective infiltration synthesis, where one of the block copolymer domains is complexed with a metal organic prior to etching. The other method includes complexing one of the domains with a metal via a solution process which not only can improve the etching resistance, but also can increase the ability to microphase separate the smaller domains. Laser ablation may be able to replace or complement these techniques. For instance, in PS-b-P2VP, where the PVP (P2VP) is complexed with a metal to increase the etching resistance, the metal can phase segregate during etching, degrading the pattern transfer. In contrast, laser ablation has proven to be gentler process for block removal.

[0011] As discussed in reviews by Lippert, laser-ablation has been used to pattern polymers down to the diffraction limit of the scanning laser since 1982. Typically the laser is in the UV range where the absorption of most polymers is high. More recently, a few authors have applied laser ablation to selectively remove blocks in block-copolymers. In this case, the resolution of the pattern is not determined by the size of the laser beam or the masking pattern, but instead by the chemical pattern in the polymer. Ahn, et. al. used an eximer laser and removed the one block that was more UV-sensitive so that, after the ablation, polystyrene dots remained. Overall, however, the final PS structure was thinner than the original. Wang, et. al. doped the PVP block of a PS-b-P4VP block copolymer to induce visible light laser ablation at 532 nm.

[0012] In various embodiments described, we build upon our previous success in selective laser ablation for dry development of a high-resolution resist material, methyl acetoxy calixarene. In our selective ablation process, we expose the calixarene using electron beam lithography and replace the wet development step with laser ablation. We found there is a difference in absorption between the exposed and unexposed regions allowing selective development of the exposed region. This selective ablation of the exposed area means the resolution is determined by the e-beam pattern, not by the laser spot size which is on the order of 300 nm FWHM. We were able to laser develop the e-beam exposed calixarene down to 15 nm half-pitch features in films thicknesses of 100 nm. The performance of the ablation was far better than that achieved by wet development. Wet development under identical electron beam expo-